

Transfer energetics of some ions based on TATB assumption in some quasi-isodielectric ethylene carbonate + water mixtures

Subrata Sinha, Sibaprasad Rudra & Kiron K Kundu*

Physical Chemistry Laboratories, Jadavpur University, Calcutta 700 032, India

Received 1 June 1992; accepted 20 July 1992

Single-ion transfer free energies, $\Delta G^\circ_{\text{t}}(i)$, and entropies, $\Delta S^\circ_{\text{t}}(i)$, of some electrolytes from water to quasi-isodielectric aqueous mixtures of 10, 30, 50 and 70 weight per cent ethylene carbonate (EC) have been determined at 35°C, using the widely used tetraphenylarsonium tetraphenylborate [$\text{Pb}_4\text{AsPh}_4\text{B}(\text{TATB})$] reference electrolyte (RE) assumption, from solubility and emf measurements at five equidistant temperatures ranging from 25° to 45°C. Analysis of $\Delta G^\circ_{\text{t}}(i)$ values of the ions as well as their chemical effects, $\Delta G^\circ_{\text{t, ch}}(i)$, as obtained after correcting for their cavity effect, estimated by the scaled particle theory (SPT) and the Born as well as ion-dipole type electrostatic effects, estimated by use of simple Born and Kim formulations respectively, reveals that cationophilicity, anionophobicity and/or predominant dispersion interactions of the solvent mixtures are guiding the solvation behaviour of the ions. But the analysis of the corresponding $T\Delta S^\circ_{\text{t, ch}}(i)$ values in the light of Kundu *et al.*'s four-step transfer process reveals that complex structural changes are guiding the entropic behaviour of these ions in these quasi-isodielectric EC-water mixtures.

It is now well recognized that ion-solvent interactions in isodielectric solvent systems have particular significance and interests¹⁻⁷. In such systems, the Born-type electrostatic effects arising from the difference of dielectric constant of the solvents being invariant, the observed transfer Gibbs free energies of ions directly reflect the short-range ion-solvent interactions relative to that in the chosen reference solvent, as are evidenced from the work of Kundu and co-workers in isodielectric protic-protic solvent system like methanol (MeOH) and propylene glycol (PgOH)¹. Similar studies in isodielectric protic-dipolar aprotic solvent system like ethylene glycol (EgOH)-acetonitrile (ACN)³, were also shown to have added interests because dipolar aprotic solvents like ACN not only show predominant anion-desolvating propensity but also interacts strongly and specifically with polarizable anions^{2,3,8-10}. Besides, studies on the standard electrode potentials (E°) of the Ag-AgCl electrode in quasi-isodielectric protic-protic EgOH-diethylene glycol (DgOH)⁵, protic-dipolar aprotic² MeOH-ACN and EgOH-N,N-dimethyl formamide (DMF)⁴ solvent mixtures were also found to directly impart important reflections on ion-solvent interactions bereft of Born-type electrostatic interactions.

Strikingly enough, similar studies with cosolvent systems iso-dielectric with water in particular, are however yet relatively few. Bates and co-workers⁶ were first to show that aqueous mixture of 50 weight

(wt.) % ethylene carbonate (EC) behaves as a 'quasi-isodielectric' protic-dipolar aprotic solvent and have reported the E° values of the Ag-AgCl electrode^{6a}, dissociation constants^{6b} of acetic and malonic acids^{6c} in that solvent at different temperatures. Moreover, recently Harakany and co-workers⁷ have reported E° values of the Ag-AgCl electrode at various composition of this quasi-isodielectric solvent system [dielectric constant ϵ , lying between 78-82 for water to 80 wt % EC at 35°C] at different temperatures, while Wells¹¹ reported the ion-solvent interactions of H^+ and Cl^- based on his exclusively own indicator method¹² at 25°C.

In the present paper we are reporting transfer energetics $\Delta Y^\circ_{\text{t}}(i)$ [$Y = \text{G}$ or S] of some ions like H^+ , K^+ , Cl^- , picrate ion (Pi^-) and $\text{Ph}_4\text{B}^-/\text{Ph}_4\text{As}^+$, from the reference solvent water to quasi-isodielectric aqueous mixtures of 10, 30, 50 and 70 wt % EC, as determined by use of the widely used $\text{Ph}_4\text{AsPh}_4\text{B}$ [TAB][Ph = phenyl] reference electrolyte (RE) assumption^{13,14}. The required $\Delta Y^\circ_{\text{t}}$ values of KBPh_4 , KPi and Ph_4AsPi as determined from solubility measurements and also of KCl as determined from the standard emf's (ΔE°) of the double cell [A]

$\text{Ag-AgCl}/\text{MCl}(m), \text{solvent}/\text{M}(\text{Hg})/\text{MCl}(m), \dots [\text{A}]$
water/AgCl-Ag

with $\text{M} = \text{K}$, were obtained in the solvent mixtures at five equidistant temperatures ranging from 25°-45°C, the corresponding data for HCl being already

known from literature⁷. Besides, ΔG° (MCl) values with $M = \text{Li, Na, Rb and Cs}$ have also been determined at 35°C by use of cell [A] with M as the respective alkali metal. These are expected to reflect the solvation behaviour of these simple alkali metal cations with varying ionic force field in the solvents.

Materials and Methods

Ethylene carbonate (KL/E. Merck) was purified by the four fractional freezings as described by Bates⁶. The melting temperature is about 309.8 K. The general experimental procedure for measuring the emf's of cell [A] were also exactly similar to those of our previous measurements¹⁵.

Methods of preparation, purification as well as the procedure for the determination of saturated solubilities at different temperatures of the salts Ph_4AsPi , Ph_4BK and KPi by spectrophotometric method were essentially similar to those described earlier¹⁵. Constancy of the absorbance to within $\pm 1\%$ was taken as the criterion of the attainment of the saturated solubility of the salt. At least two sets of measurements were made for all the solutes and the results were found to agree to within 1%. Since the saturated solutions of the salts were appropriately diluted by water, the maximum wave length and the molar extinction coefficient values of the

salts were the same as those in water and as taken in our previous papers¹⁵.

Results

The observed saturated solubilities (S) in mol dm^{-3} for the salts KBPh_4 , Ph_4AsPi and KPi are given in Table 1. The negative logarithms of the solubility product, pK_{sp} , of the salts and the free energies of solution on molar scale at different temperatures were computed by using the relation

$$\Delta G_s^\circ = -2 RT \ln S \gamma_{\pm} = 2.303 RT pK_{sp}^\circ \quad \dots (1)$$

where $\gamma_{\pm}$ is the mean molar activity coefficient of the electrolyte and was computed by use of extended Debye-Hückel equation using as before¹⁵ the ion size parameter $a_{K^+}^\circ = a_{Pi^-}^\circ = 0.3 \text{ nm}$ and $a_{Ph_4B^-}^\circ = a_{Ph_4As^+}^\circ = 0.5 \text{ nm}$ and the required values of density (d_s) and the dielectric constant (ϵ_s) and the Debye-Hückel constants at different temperatures being taken from literature⁷. The pK_{sp}° and ΔG_s° values for the solvents so obtained are presented in Table 1. The ΔG_s° values at different temperatures were then fitted by the method of least squares to the equation of the form

$$\Delta G_s^\circ = a + bT + cT \ln T \quad \dots (2)$$

The values of the coefficients a , b and c are presented in Table 2. The values of standard transfer ener-

Table 1—Solubility (S) in mol dm^{-3} , solubility product (K_{sp}°) and mean activity coefficients $\gamma_{\pm}$ of Ph_4AsPi , Ph_4BK and KPi in EC + water mixtures at different temperatures

Solute		10 wt. % EC					30 wt. % EC				
		25	30	35	40	45	25	30	35	40	45°C
Ph_4AsPi	$S \times 10^5$	9.838	12.218	15.191	18.227	21.806	131.5	149.34	170.14	224.29	308.16
	$\gamma_{\pm}$	0.995	0.995	0.994	0.994	0.994	0.993	0.992	0.992	0.992	0.992
	pK_{sp}°	8.02	7.83	7.54	7.48	7.33	5.77	5.66	5.55	5.31	5.03
	$S \times 10^5$	43.538	51.843	59.79	71.373	82.938	542.86	585.77	664.02	790.71	952.38
Ph_4BK	$\gamma_{\pm}$	0.993	0.993	0.993	0.993	0.993	0.992	0.991	0.991	0.991	0.991
	pK_{sp}°	6.73	6.58	6.45	6.30	6.17	4.54	4.47	4.36	4.21	4.05
	S	0.0365	0.0415	0.0493	0.0592	0.0731	0.1075	0.1165	0.1299	0.1496	0.1775
	$\gamma_{\pm}$	0.988	0.987	0.987	0.986	0.986	0.984	0.984	0.983	0.982	0.981
KPi	pK_{sp}°	2.89	2.78	2.63	2.47	2.29	1.95	1.80	1.79	1.67	1.57
		50 wt. % EC					70 wt. % EC				
		25	30	35	40	45	25	30	35	40	45°C
Ph_4AsPi	S	0.0127	0.0136	0.0150	0.0167	0.0189	0.0610	0.0649	0.0694	0.0735	0.0780
	$\gamma_{\pm}$	0.991	0.991	0.991	0.991	0.990	0.988	0.987	0.987	0.987	0.986
	pK_{sp}°	3.80	3.74	3.66	3.56	3.46	2.44	2.39	2.33	2.28	2.23
	S	0.0445	0.0460	0.0479	0.0508	0.0548	0.1188	0.1237	0.1236	0.1399	0.1399
Ph_4BK	$\gamma_{\pm}$	0.989	0.989	0.989	0.989	0.988	0.984	0.983	0.983	0.982	0.982
	pK_{sp}°	2.71	2.68	2.65	2.60	2.53	1.87	1.83	1.80	1.72	1.72
	S	0.2190	0.2299	0.2469	0.2698	0.2938	0.3062	0.3198	0.3389	0.3753	0.4155
	$\gamma_{\pm}$	0.978	0.997	0.976	0.975	0.974	0.969	0.968	0.967	0.965	0.962
KPi	pK_{sp}°	1.34	1.30	1.24	1.16	1.09	1.06	1.02	0.97	0.88	0.80

getics like ΔG_t° and ΔS_t° of the salts at 35°C were calculated on the mole fraction scale using the relations

$$\Delta G_t^\circ = {}_s\Delta G_s^\circ - {}_w\Delta G_s^\circ = 2.303 RT [p_s K_{sp}^c - p_w K_{sp}^c] - 2 RT \ln (M_s d_w / M_w d_s) \quad \dots (3)$$

$$= (a_s - a_w) + (b_s - b_w)T + (c_s - c_w)T \ln T - 2 RT \ln (M_s d_w / M_w d_s) \quad \dots (3')$$

and

$$\Delta S_t^\circ = (b_w - b_s) + (c_w - c_s)(1 + \ln T) + 2 R \ln (M_s d_w / M_w d_s) + 2 RT (d \ln d_w / dT - d \ln d_s / dT) \quad \dots (4)$$

The subscripts *s* and *w* refer to cosolvent and water respectively. The required values of temperature coefficient of densities, $d \ln d_s / dT$, were obtained from literature⁷. The values thus obtained are given in Table 2.

For KCl the observed emf (ΔE) values of cell [A] at different molalities *m* (mol kg⁻¹) in different solvent mixtures at three different temperatures 25, 35 and 45°C and those of other alkali metal chlorides at 25°C are given in the Appendix I. As in previous studies¹⁵⁻¹⁷, the standard ΔE° values were obtained by extrapolating the observed linear plots of the function $\Delta E'$, defined by Eq. (5), against *m* to *m* = 0

$$\Delta E' \equiv \Delta E - 2 k [{}_s f(m) - {}_w f(m)] = \Delta E^\circ - 2 k \Delta b. m. \quad \dots (5)$$

where the symbols have their usual significance as indicated therein¹⁵⁻¹⁷. The required solvent parameters like density and dielectric constant and the involved Debye-Hückel constants at different temperatures were taken from literature⁷. The estimated average uncertainties in ΔE° values are ± 0.3 mV.

Standard free energies of transfer, ΔG_t° , of KCl as well as other MCl salts from water to the mixed solvents on mole fraction scale were obtained at each temperature for KCl and at 35°C for other MCl salts by use of Eq. (6).

$$\Delta G_t^\circ = F \Delta E^\circ - 2 RT \ln (M_s / M_w) \quad \dots (6)$$

where *M_w* and *M_s* are the molar and mean molar mass of pure water and the solvent mixtures respectively. The ΔG_t° (KCl) values at different temperatures were then fitted to Eq. (7).

$$\Delta G_t^\circ = A + BT + CT \ln T \quad \dots (7)$$

where A, B and C are constants. The values of ΔS_t° on mole fraction scale were obtained by Eq. (8).

$$\Delta S_t^\circ = -[B + C(1 + \ln T)] \quad \dots (8)$$

The values of A, B and C along with ΔG_t° and ΔS_t° at 35°C are listed in Table 3. As before^{19a}, the estimated uncertainties in ΔG_t° and ΔS_t° lie within ± 0.03 kJ mol⁻¹ and ± 2 J K⁻¹ mol⁻¹ respectively. These values were then utilised to compute the individual ion contributions by the widely used TATB reference electrolyte assumption^{10,13,14} using the

Table 2—Coefficients a, b and c in Eq. (2) for Ph₄AsPi, Ph₄BK and KPi in EC + water mixtures and transfer energetics (ΔG_t° and $T\Delta S_t^\circ$) of the salts from water to aquo-EC solvents at 35°C (mole fraction scale)

Solutes	a (kJ mol ⁻¹)	b (kJ mol ⁻¹ K ⁻¹)	c (kJ mol ⁻¹ K ⁻¹)	ΔG_t° (kJ mol ⁻¹)	$T\Delta S_t^\circ$ (kJ mol ⁻¹)
10 wt. % EC					
Ph ₄ AsPi	235.0493	-3.8221	0.5594	-6.24	19.71
Ph ₄ BK	-12.5525	1.3412	-0.2054	-6.02	37.33
KPi	-540.3842	12.8785	-1.9325	-2.88	2.37
30 wt. % EC					
Ph ₄ AsPi	-153.0934	34.7934	-5.1861	-19.42	37.70
Ph ₄ BK	-791.7616	18.2191	-2.7163	-18.95	45.10
KPi	-634.6174	14.6321	-2.1880	-8.62	-7.07
50 wt. % EC					
Ph ₄ AsPi	-370.0839	8.7432	-1.3039	-31.35	14.35
Ph ₄ BK	-298.3225	6.8706	-1.0211	-29.95	27.33
KPi	-268.3445	6.3203	-0.9468	-12.73	-19.00
70 wt. % EC					
Ph ₄ AsPi	19.3051	-0.0176	-7.37×10^{-5}	-40.52	11.59
Ph ₄ BK	86.3265	-1.5898	0.2345	-36.40	31.98
KPi	-454.9238	10.3987	-1.5538	-15.71	-15.09

^aValues for a, b & c of water are taken as given in ref. 19(a).

Table 3—Coefficients A, B and C in Eq. 7 for KCl in EC + H₂O mixtures and transfer energetics (ΔG_i° and $T\Delta S_i^\circ$) of the salt from water to EC + H₂O mixtures at 35°C (mole fraction scale)

Wt. % EC	KCl				
	A (kJ mol ⁻¹)	B (kJ mol ⁻¹ K ⁻¹)	C (kJ mol ⁻¹ K ⁻¹)	ΔG_i° (kJ mol ⁻¹)	$T\Delta S_i^\circ$ (kJ mol ⁻¹)
10	61.3192	-1.3766	0.2056	-0.26	-1.77
30	10.3077	-0.3212	0.0510	-0.08	-5.33
50	138.1085	-3.1638	0.4757	0.81	-9.30
70	-263.7319	5.6493	-0.8325	2.84	-10.05

Table 4—Values of standard free energies of transfer, $\Delta G_i^\circ(i)$ and entropies of transfer $T\Delta S_i^\circ(i)$ (mole fraction scale) in kJ mol⁻¹ of individual ions from water to EC + H₂O mixtures at 35°C

Ions	10 wt. % EC		30 wt. % EC		50 wt. % EC		70 wt. % EC	
	$\Delta G_i^\circ(i)$	$T\Delta S_i^\circ(i)$	$\Delta G_i^\circ(i)$	$T\Delta S_i^\circ(i)$	$\Delta G_i^\circ(i)$	$T\Delta S_i^\circ(i)$	$\Delta G_i^\circ(i)$	$T\Delta S_i^\circ(i)$
Ph ₄ B ⁺ /Ph ₄ As ⁺	-4.7	27.3	-14.9	44.9	-24.3	30.3	-30.6	29.3
K ⁺	-1.3	10.0	-4.1	0.2	-5.7	-3.0	-5.8	2.7
H ⁺	-1.1	11.7	-4.1	3.4	-5.9	-1.9	-6.1	-5.3
Pi ⁻	-1.6	-7.6	-4.5	-7.2	-7.1	-16.0	-9.9	-17.7
Cl ⁻	1.1	-11.8	4.0	-5.5	6.5	-6.3	8.6	-12.7

Table 4a—Values of standard free energies of transfer $\Delta G_i^\circ(i)$ (mole fraction scale) in kJ mol⁻¹ of individual ions from water to EC + H₂O mixtures at 25°C

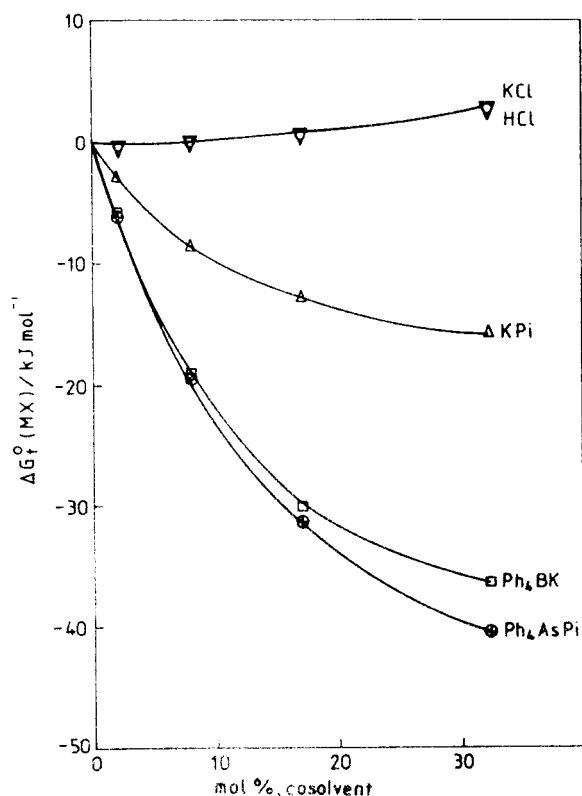
Wt. % EC	$\Delta G_i^\circ(i)$				
	Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺
10	-1.5	-1.7	-1.3	-1.4	-1.4
30	-3.6	-4.5	-4.1	-4.5	-4.7
50	-4.3	-4.6	-5.9	-6.4	-6.9
70	-3.4	-3.9	-5.9	-6.9	-7.3

usual formulations as before¹⁵ and the evolved ΔG_i° and ΔS_i° values of the involved salts. For computing the transfer energetics of H⁺ and Cl⁻, the values of ΔG_i° (HCl) and ΔS_i° (HCl) were taken from literature⁷. The values of $\Delta Y_i^\circ(i)$ thus obtained are listed in Table 4. In Table 4a the values of standard free energies of transfer $\Delta G_i^\circ(i)$ (mole fraction scale) in kJ mol⁻¹ of individual ions from water to EC + H₂O mixtures at 25°C are given

Discussion

Free energies of transfer

ΔG_i° -composition profiles at 35°C for the RE salts, KCl and HCl are illustrated in Fig. 1. From the figure it appears that the salts like KBPh₄, Ph₄AsPi and KPi are increasingly stabilized, while KCl and HCl are increasingly destabilized. Seemingly, organic ions are increasingly stabilized due to the increased dispersion interaction with the large sized highly polarizable organic cosolvent molecules. However, as indicated in our previous papers¹⁵, the discussions on $\Delta G_i^\circ(i)$ values of the ions rather than

Fig. 1—Variation of $\Delta G_i^\circ(MX)$ of some electrolytes with composition at 35°C in quasi-isodielectric aqueous ethylene carbonate solvent system

that of the electrolyte, being more informative regarding the involved ion-solvent interaction, $\Delta G_i^\circ(i)$ -composition profiles of the ions of those electrolytes as well as of other alkali metal chlorides at 35°C are illustrated in Fig. 2.

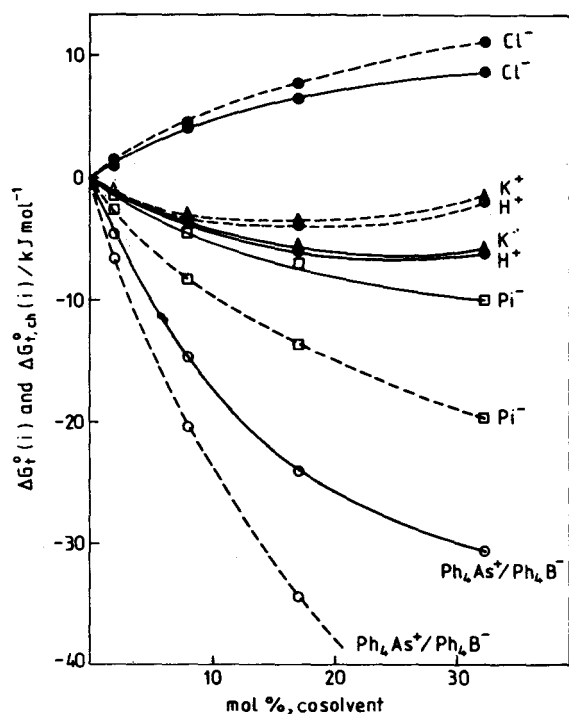


Fig. 2—Variation of $\Delta G^\circ_{t,i}$ and $\Delta G^\circ_{t,ch,i}$ of some ions with composition at 35°C in quasi-isodielectric aqueous ethylene carbonate solvent system

Now, although the nature of the $\Delta G^\circ_{t,i}$ -composition profiles of H⁺ and Cl[−] are more or less same as that of the previous results of Wells¹¹, the relative magnitudes of $\Delta G^\circ_{t,i}$ values for H⁺ and Cl[−] are slightly different as given below

$$\Delta G^\circ_{t,i} \text{ at } 25^\circ\text{C}/\text{kJ mol}^{-1}$$

	10 wt % EC		30 wt % EC		50 wt % EC	
	H ⁺	Cl [−]	H ⁺	Cl [−]	H ⁺	Cl [−]
TATB method	−1.1	1.0	−4.1	4.0	−5.9	6.5
Wells method	−2.3	2.3	−6.3	6.1	−8.1	8.5

However, the observed discrepancies in the magnitudes obtained by the different extra-thermodynamic assumptions such as these, in different solvent systems are of course quite usual. But as Blandamer and co-workers¹⁸ and also Marcus¹⁴ have recently pointed out, there exists some shortcomings in the Wells' method. True, Wells in a subsequent paper^{12c} has critically examined his method in relation to some of the criticisms of Blandamer *et al.*¹⁸ and seemingly cleared out some of the points raised. But it is debatable if all the assumptions involved therein are valid irrespective of the nature and concentrations of the cosolvents. In fact it appears that Wells' solvent sorting procedure for evolving $\Delta G^\circ_{t,i}(\text{H}^+)$ is an involved problem especially because of unique

physico-chemical behaviour of H⁺ in respect of H₂O and other amphiprotic solvents in particular. So, as Marcus¹⁴ from a detailed critical analysis of the relative merits and demerits of different extra-thermodynamic assumptions pointed out, despite some intrinsic defects TATB reference electrolyte method has the strongest conceptual basis and amongst the various extra-thermodynamic assumptions weighted TATB assumption is relatively more reasonable, though not beyond criticism, and hence the data derived thereof are more meaningful.

Now as has been increasingly recognized^{14,15}, the $\Delta G^\circ_{t,i}$ value of any ion may be visualized as consisting of cavity, electrostatic and chemical interaction terms i.e.,

$$\Delta G^\circ_{t,i} = \Delta G^\circ_{t,cav,i} + \Delta G^\circ_{t,el,i} + \Delta G^\circ_{t,ch,i} \quad \dots (9)$$

While $\Delta G^\circ_{t,cav,i}$ stands for the difference of free energy changes involved in creating appropriate cavities for accommodating the ion in the reference solvent water (w) and the concerned solvent (s), $\Delta G^\circ_{t,el,i}$ stands for the corresponding terms^{19,20} associated chiefly with Born-type interaction, $\Delta G^\circ_{t,B,i}$ and the ion-dipole interaction, $\Delta G^\circ_{t,i-d,i}$, the corresponding ion-induced dipole interaction term, $\Delta G^\circ_{t,i-id,i}$ being usually fairly small as compared to that for ion-dipole interactions²¹. Moreover, the possible ion-quadrupole interaction term, $\Delta G^\circ_{t,i-q,i}$, though not feasible to compute in this case because of nonavailability of quadrupolar moment of EC molecules, usually hardly exceeds 10% of the total electrostatic terms as indicated by Marcus^{14,17} and hence might be taken as negligible. The rest $\Delta G^\circ_{t,ch,i}$ term, tacitly referred to as the chemical effect, in fact stands for all the other effects such as that arising from short-range interactions, specific or otherwise, and the structural interaction effect that arises from the changes of the solvent structure induced by the ions, if any, apart from that involved in the cavity effect. Notably, as indicated in our previous papers^{17,19c}, accounting of the effects of possible selective/preferential solvation of ions as well as the structural interaction term being an involved problem, it is not feasible to dissect the same from $\Delta G^\circ_{t,ch,i}$, although ideas about the same might be derived in course of the discussion of the behaviour of $\Delta G^\circ_{t,ch,i}$. So, the discussion of the behaviour of $\Delta G^\circ_{t,ch,i}$ with cosolvent composition should be more informative and useful.

Consequently, as before²⁰, we have tentatively computed cavity forming effect, $\Delta G^\circ_{t,cav,i}$ by the scaled particle theory (SPT)²¹ using the formulations described earlier^{19,20}, Born-type electrostatic effect, $\Delta G^\circ_{t,B,i}$ by simple Born equation²² and the ion-dipole interaction term $\Delta G^\circ_{t,i-d,i}$ by using the

formulations of Kim²³. Now the values of $\Delta G_{t,cav}^\circ(i)$, $\Delta G_{t,B}^\circ(i)$ and $\Delta G_{t,i-d}^\circ(i)$ when subtracted from the $\Delta G_t^\circ(i)$ values yielded the values of $\Delta G_{t,ch}^\circ(i)$, which are listed in Table 5 and illustrated in Fig. 2 by dotted lines.

From the perusal of Table 5 and Fig. 2 we find that as expected for these quasi-isodielectric solvents, $\Delta G_{t,B}^\circ$ values are fairly small, while those for $\Delta G_{t,i-d}^\circ(i)$ are fairly large because of the large dipole moment [$\mu = 4.87$ D¹⁰ of the cosolvent EC molecule]. Also, for small sized ions (cations and anions) cavity effect is small and gets nullified by the opposing electrostatic effect. But for large sized ions contributions of cavity effect are large. Thus,

$\Delta G_{t,ch}^\circ(i)$ -composition profile of H^+ reflects the increased basicity¹⁷ of this solvent system at water-rich region, which at higher wt % of EC becomes almost constant. This is probably due to the fact that at low compositions of EC, EC molecules are free to solvate the incoming cations through the enhanced

formal negative charge on the $\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{C}=\text{O} \\ \diagdown \quad \diagup \\ \text{O} \end{array}$ group

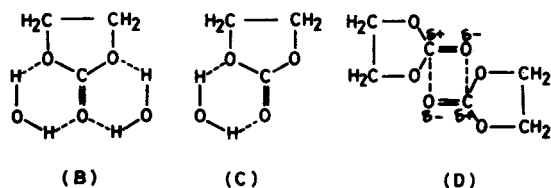
or through that induced by this group on the O-centres of H-bonded H_2O molecules forming H-bonded $EC-(H_2O)_x$ complexes⁷ [see the structures B and C]. This in fact reflects that addition of EC

Table 5—Values of free energies and enthalpies of cavity formation ($\bar{G}_c^\circ$) and ($\bar{H}_c^\circ$) and standard free energies of transfer $\Delta G_{t,cav}^\circ(i)$, $\Delta G_{t,B}^\circ(i)$, $\Delta G_{t,i-d}^\circ(i)$ and $\Delta G_{t,ch}^\circ(i)$ and entropies of transfer $\Delta S_{t,cav}^\circ(i)$, $\Delta S_{t,B}^\circ(i)$ and $\Delta S_{t,ch}^\circ(i)$ (mole fraction scale) in kJ mol^{-1} of the individual ions from water to EC + water mixtures at 35°C

Ions	$\bar{G}_c^\circ$ (water)	$\bar{G}_c^\circ$ (solvent)	$\bar{H}_c^\circ$ (water)	$\bar{H}_c^\circ$ (solvent)	$\Delta G_{t,cav}^\circ(i)^a$	$\Delta G_{t,B}^\circ(i)^b$	$\Delta G_{t,i-d}^\circ(i)^d$	$\Delta G_{t,ch}^\circ(i)$	$\Delta S_{t,cav}^\circ(i)^a$	$\Delta S_{t,B}^\circ(i)^b$	$\Delta S_{t,ch}^\circ(i)$
10 wt. % EC											
$\text{Ph}_4\text{As}^+ / \text{Ph}_4\text{B}^-$	93.6	95.8	25.2	26.9	2.1	0.0	-0.2	-6.6	-0.5	0.3	27.5
K^+	13.1	13.5	3.2	3.4	0.2	-0.1	-0.4	-1.0	0.0	0.8	9.2
H^+	13.9	14.3	3.4	3.6	0.3	-0.1	-0.4	-0.9	0.0	0.4	11.3
Pi^-	69.0	70.6	18.4	19.6	1.5	0.0	-0.3	-2.8	-0.3	0.3	-7.6
Cl^-	21.2	21.8	5.4	5.7	0.4	-0.1	-0.4	1.2	-0.1	0.6	-12.3
30 wt. % EC											
$\text{Ph}_4\text{As}^+ / \text{Ph}_4\text{B}^-$		100.8		46.4	6.5	-0.1	-0.8	-20.5	14.2	0.4	30.3
K^+		14.3		5.9	0.7	-0.2	-1.5	-3.1	2.1	1.2	-3.1
H^+		15.1		6.2	0.8	-0.1	-1.5	-3.3	2.2	0.6	0.6
Pi^-		74.4		33.8	4.9	-0.1	-1.0	-8.3	10.7	0.4	-18.3
Cl^-		23.0		9.8	1.3	-0.2	-1.5	4.4	3.3	0.9	-9.7
50 wt. % EC											
$\text{Ph}_4\text{As}^+ / \text{Ph}_4\text{B}^-$		100.7		63.4	11.9	-0.1	-1.6	-34.5	25.7	0.5	4.1
K^+		15.3		8.0	1.2	-0.4	-3.1	-3.4	3.8	1.7	-8.5
H^+		16.1		8.5	1.3	-0.2	-3.1	-3.9	4.0	0.8	-6.7
Pi^-		78.7		46.3	8.8	-0.1	-2.2	-13.6	19.3	0.6	-35.9
Cl^-		24.5		13.4	2.3	-0.3	-3.1	7.6	6.0	1.3	-13.6
70 wt. % EC											
$\text{Ph}_4\text{As}^+ / \text{Ph}_4\text{B}^-$		114.8		110.6	19.2	-0.2	-3.1	-46.5	64.8	0.4	-35.9
K^+		16.6		13.9	1.9	-0.5	-5.9	-1.3	9.3	1.3	-7.9
H^+		17.5		14.8	2.1	-0.3	-5.9	-2.0	9.8	0.6	-15.7
Pi^-		84.8		80.7	14.2	-0.2	-4.2	-19.7	48.5	0.5	-66.7
Cl^-		26.5		23.4	3.7	-0.4	-5.9	11.2	14.8	1.0	-28.5

^aThe required diameter (b) of the solvent constituents and the value of dipole moment of EC are taken as given in ref. 10 and those for the solute species $b_{\text{Ph}_4\text{B}^-} = 0.84$ nm^{19a}, $b_{\text{Pi}^-} = -0.72$ nm³⁷, $b_{\text{Cl}^-} = 0.362$ nm¹⁰, $b_{\text{K}^+} = 0.266$ nm¹⁰ and $b_{\text{H}_3\text{O}^+} = 0.276$ nm^{19d}.

^bThe required radii of the ionic species are obtained from the corresponding diameter of the species as indicated in 'a' and that of H^+ as equal to 0.276 nm^{19d}.



initially causes breakdown²⁴ of 3D structures of water, which induces increased basicity of the solvents. But with increased concentration of EC possible formation of EC-EC aggregates [see structure D], similar to that in acetonitrile^{15b}, possibly takes place^{7,11} and as a result the solvation of H⁺ and K⁺ remains more or less constant. Due to the above structural features desolvation of Cl⁻ seemingly increases with the increased composition of dipolar aprotic EC in consonance with the well recognized fact that dipolar aprotic solvents are generally anion desolvator^{8,10}.

On the other hand, the increasingly negative magnitudes of $\Delta G_{t, ch}^{\circ}(i)$ -composition profile for Ph₄B⁻/Ph₄As⁺ can be attributed, as in the other cosolvent systems^{15b,c, 25}, to the dispersion interactions of four phenyl groups with the present highly polarizable cosolvent molecules [$\alpha_{EC} = 6.69 \times 10^{-24} \text{ cm}^3$ as compared to $\alpha_w = 1.46 \times 10^{-24} \text{ cm}^3$]¹⁰. As indicated by various authors^{3,5,25}, although dipolar aprotic solvents are anion desolvators, these often interact strongly and specifically with large polarizable anions as is seemingly true in the case of Ph₄B⁻ and Pi⁻ ions.

That the dispersion and soft-soft interactions²⁶ play an important role in this aquo-cosolvent system is also vividly reflected in the $\Delta G_{t, ch}^{\circ}(i) - r_i^{-1}$ profiles for all the four compositions of the solvents [vide, Fig. 3]. A perusal of the profiles indicates that as have been observed in aqueous mixtures of MeOH²⁷, DMSO^{28a}, urea^{28b}, methoxy ethanol^{15d} and dimethoxy ethane^{15c}, with the increase of cosolvent composition the sharp drops in $\Delta G_{t, ch}^{\circ}(i)$ values with the increased size of the cations are essentially indicative of the fact that increasingly large sized cations like Rb⁺ and Cs⁺ result in soft-soft interactions²⁶ with the large sized and highly polarizable EC cosolvent molecules. The latter interaction being superimposed with other types of interactions results in the observed profiles. The unusual breaks in these profiles are possibly indicative of the effect of structural changes of the solvents.

Entropies of transfer

Figure 4 depicts the $T\Delta S_{t, ch}^{\circ}$ -composition profiles of some salts at 35°C. Interestingly enough, while the profiles for the large-sized salts exhibit roller-

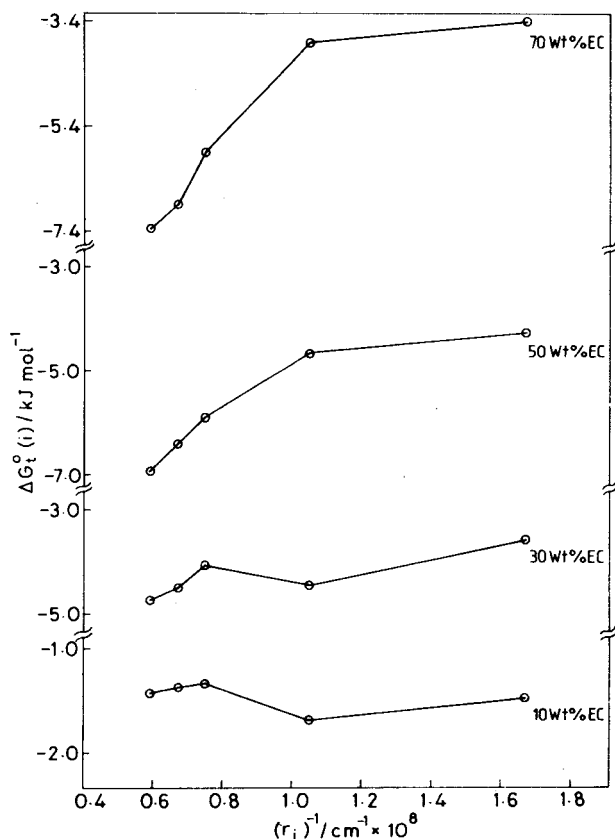


Fig. 3—Variation of $\Delta G_{t, ch}^{\circ}(i)$ of M^+ ($M = \text{Li, Na, K, Rb \& Cs}$) at 25°C with $(r_M)^{-1}$ in different compositions of quasi-isodielectric aqueous ethylene carbonate solvent system

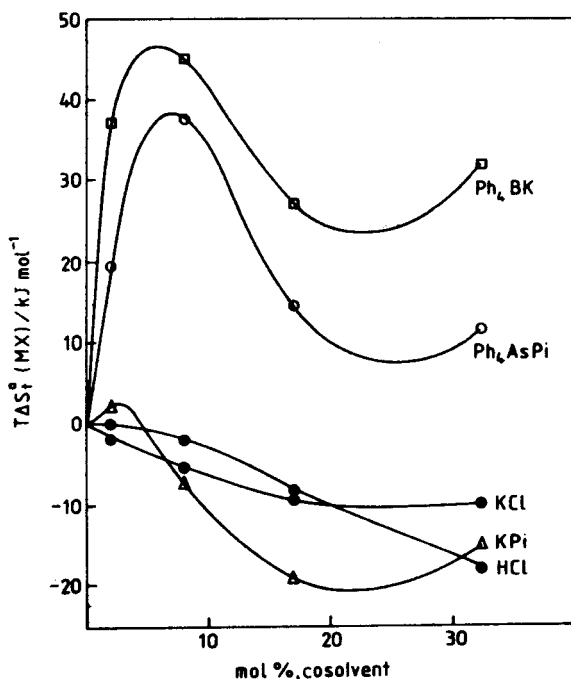


Fig. 4—Variation of $T\Delta S_{t, ch}^{\circ}(MX)$ of some electrolytes MX with composition at 35°C in quasi-isodielectric aqueous ethylene carbonate solvent system

coaster type behaviour, those for the small sized ionic salts show more or less monotonic variation. Seemingly, the effects of structural changes of the solvents involved, especially for large-sized species, are fairly significant. However, as indicated in our previous papers¹⁹, since the discussion of $T\Delta S_i^\circ(i)$ values of single ions rather than those of the electrolytes should be more informative, $T\Delta S_i^\circ(i)$ composition profiles of the ions are illustrated in Fig. 5 at 35°C. Notably, as in other aquo-organic^{19b,29-35} and aquo-ionic^{19a} solvent systems the profiles for cation (H^+ and K^+) exhibit roller-coaster type behaviour with a maximum around 3-4 mol % EC, while those for anions (Cl^- , PI^-) pass through a minimum. But that for Ph_4B^- , as in urea-water mixtures^{19b}, exhibits a maximum around 4-5 mol % followed by a downward trend.

In the previous papers^{19a,b} this type of opposite behaviour for the small cations and anions has been discussed satisfactorily in the light of Kundu *et al.*'s four-step transfer process³⁶. Here as well, before attempting to understand the same for this solvent system let us at first make a tentative estimate of $\Delta S_{t, ch}^\circ(i)$ for the ions which would be obtained by subtracting $\Delta S_{t, cav}^\circ(i)$ ³⁷ and $\Delta S_{t, B}^\circ(i)$ ³⁶ values from the corresponding values of $\Delta S_i^\circ(i)$, exactly similar

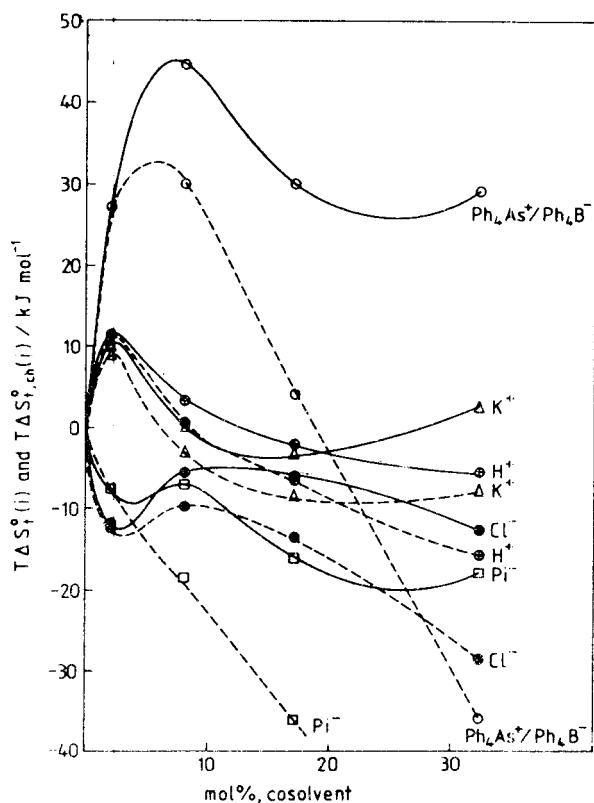


Fig. 5—Variation of $T\Delta S_i^\circ(i)$ and $T\Delta S_{t, ch}^\circ(i)$ of some ions with composition at 35°C in quasi-isodielectric aqueous ethylene carbonate solvent system

to what have been done in the previous papers^{19a,b,37}. The calculated values are shown in Table 5 and illustrated in Fig. 5 by dotted lines. Strikingly enough, there are little differences between $T\Delta S_i^\circ(i)$ and $T\Delta S_{t, ch}^\circ(i)$ -composition profiles in water-rich region but the differences increase with the increased composition of EC.

Now according to Kundu *et al.*'s four-step transfer process³⁶

$$\Delta S_{t, ch}^\circ(i) = \Delta S_1^\circ - \Delta S_2^\circ + \Delta S_3^\circ - \Delta S_4^\circ$$

The significance of the four steps have been discussed in our previous papers^{36,19}. Thus, in short while ΔS_1° is the entropy change involved in step 1 for releasing free ion (i) from its hydration cosphere and $-\Delta S_2^\circ$ is the entropy change involved in step 2 for the formation of three dimensional (3D) water structure from the water molecules to be released from the hydration cosphere, ΔS_3° is that for step 3 accompanying the breakdown of the 3D water structure, if any, in the aqueous cosolvent mixtures to release the water/cosolvent molecules required in step 4 for solvating the transferred ion, wherein the entropy change involved is $-\Delta S_4^\circ$. Now for the transfer of a particular ion steps (1) and (2) being related to water, each of the quantities $\Delta S_1^\circ, -\Delta S_2^\circ$ and their sum ($\Delta S_1^\circ - \Delta S_2^\circ$) is constant, while $\Delta S_3^\circ, -\Delta S_4^\circ$ and their sum ($\Delta S_3^\circ - \Delta S_4^\circ$) being related to the solvents other than water vary with cosolvent composition.

As indicated earlier^{15f,15a}, small cations like H^+ and K^+ being highly hydrated, $(\Delta S_1^\circ - \Delta S_2^\circ)$ will be a constant positive quantity for each ion. On the other hand, anions like Cl^- being larger in size are generally less hydrated due to low ionic force field and designated as 3D water structure breaker for the large secondary solvation zone (SSZ) round them is having more disorder. Consequently, the net contribution $(\Delta S_1^\circ - \Delta S_2^\circ)$ will be a constant negative quantity for the anions like Cl^- .

Now since the addition of small amounts of EC to water seemingly causes the breakdown of the characteristic 3D structure of water²⁴, at the initial water-rich regions of EC-water mixtures comparatively more monomeric water and EC molecules are free to solvate the incoming cations and so $\Delta S_3^\circ \approx 0$, but $-\Delta S_4^\circ$, the entropy change in step 4 would be increasingly negative since H^+ and K^+ are likely to induce more order for the formation of solvated ionic species in the cosolvent. Thus $T\Delta S_{t, ch}^\circ(i)$ -composition profiles for the cations pass through a maxima, as observed. But at higher compositions of EC when the free monomeric water and EC molecules are engaged in possible H-bonded $EC + 2H_2O$ clusters (structure B and C) and EC-EC dimeric aggre-

gates (see structure D), ΔS_3° will become increasingly positive and so also the composite term $(\Delta S_3^\circ - \Delta S_4^\circ)$ which on addition with $(\Delta S_1^\circ - \Delta S_2^\circ)$ gives rise to a positive trend of the said profiles, as observed.

Similarly, for anions, ΔS_3° would be zero at initial compositions. Again as the anions are likely to induce some order in step 4, ΔS_4° will be increasingly negative. Consequently, the net contribution of the four steps will form an increasing negative trend of $T\Delta S_{t, ch}^\circ(i)$ -composition profiles at initial compositions of EC. But after about 4 mol % EC where the free species are likely to be progressively replaced by possible H-bonded EC + H₂O complexes^{7,11} [B.C.], ΔS_3° would be increasingly positive due to the possible breakdown of the EC + H₂O complexes into free H₂O and EC molecules. As a result, at higher compositions of EC $(\Delta S_3^\circ - \Delta S_4^\circ)$ would become increasingly positive and consequently, the opposing effects of $(\Delta S_1^\circ - \Delta S_2^\circ)$ and $(\Delta S_3^\circ - \Delta S_4^\circ)$ will result in a minimum in $T\Delta S_{t, ch}^\circ(i)$ -composition profile for the anion like Cl⁻. But at still higher compositions (> 10 mol % EC) the observed negative trend of the profile of Cl⁻ ion is possibly indicative of the usual superimposed effect of packing imbalance in the bulk of the mixed solvents³⁶, which overcomes the effect of EC + H₂O complexes^{3,6} [B.C.]. K⁺ being smaller in size, the downward trend due to the corresponding packing imbalance effect is not perceptible at this experimental terminal composition though that for larger sized H₃O⁺ is being exhibited.

The increased negative trend of $T\Delta S_{t, ch}^\circ(i)$ -composition profile of Pi⁻ from the initial composition is possibly due to the fact that Pi⁻ being larger in size its ionic force field is small and consequently, it cannot breakdown either the EC + H₂O clusters or EC-EC aggregates and as a result $\Delta S_3^\circ \approx 0$ all along. And the increased solvation of Pi⁻ due to dispersion interactions by cosolvent EC molecules and the accompanying increasing magnitudes at $-\Delta S_4^\circ$, will impart increasingly negative trend of $\Delta S_{t, ch}^\circ(i)$, as observed.

For the large-sized Ph₄B⁻ however, transfer to the mixed solvents leads to an initial increase in $T\Delta S_{t, ch}^\circ$ values followed by a sharp decrement at higher compositions. The initial increase is indicative of the fact that just as small-sized hydrophilic cations due to hydration of the first kind^{38,39} accompanying large negative entropy change will impart large positive $(\Delta S_1^\circ - \Delta S_2^\circ)$ value. The latter is seemingly overcome by the increasingly negative magnitudes of $(\Delta S_3^\circ - \Delta S_4^\circ)$ as caused partly by increasing dispersion interactions due to large sized cosolvent EC molecules and partly by the effect of packing imbalance, as is usual especially at higher compositions of the mixed solvents, and thus result in the observed initial maximum in $\Delta S_{t, ch}^\circ(i)$ composition profile followed by the sharp downward fall.

Acknowledgement

We wish to thank the UGC, New Delhi for financial assistance and granting an SRF to one of us, S S.

Appendix: The observed emf values in volt of cell [A]-Ag:AgCl/MCl(m), Solvent/M(Hg)/MCl(m), Water/AgCl-Ag with M = K

25°C		35°C		45°C	
$m(\text{mol kg}^{-1})$	ΔE	$m(\text{mol kg}^{-1})$	ΔE	$m(\text{mol kg}^{-1})$	ΔE
10 wt. % EC					
0.1210	0.0029	0.1144	0.0026	0.1479	0.0039
0.1015	0.0025	0.1035	0.0026	0.1229	0.0036
0.0810	0.0022	0.0804	0.0024	0.1061	0.0036
0.0602	0.0020	0.0617	0.0022	0.0826	0.0035
0.0433	0.0018	0.0493	0.0021	0.0655	0.0034
0.0201	0.0016	0.0260	0.0019	0.0449	0.0032
$\Delta E^\circ = 0.00135$		$\Delta E^\circ = 0.00175$		$\Delta E^\circ = 0.00287$	
30 wt. % EC					
0.1104	0.0130	0.1130	0.0145	0.1421	0.0187
0.0957	0.0128	0.0904	0.0142	0.1181	0.0177
0.0763	0.0125	0.0784	0.0141	0.0985	0.0176
0.0570	0.0124	0.0571	0.0140	0.0823	0.0174
0.0404	0.0120	0.0381	0.0139	0.0593	0.0170
0.0188	0.0116	0.0185	0.0136	0.0368	0.0166
$\Delta E^\circ = 0.0115$		$\Delta E^\circ = 0.0135$		$\Delta E^\circ = 0.0160$	

(Contd)

Appendix: The observed emf values in volt of cell $\{A\} - Ag: AgCl / MCl(m), \text{Solvent} / M(Hg) / MCl(m),$
 Water / $AgCl - Ag$ with $M = K$ — (Contd)

25°C		35°C		45°C			
$m(\text{mol kg}^{-1})$	ΔE	$m(\text{mol kg}^{-1})$	ΔE	$m(\text{mol kg}^{-1})$	ΔE		
50 wt. % EC							
0.1198	0.0334	0.1106	0.0370	0.1145	0.0427		
0.1012	0.0330	0.0918	0.0365	0.0938	0.0423		
0.0809	0.0330	0.0757	0.0364	0.0761	0.0418		
0.0594	0.0326	0.0563	0.0360	0.0588	0.0418		
0.0202	0.0320	0.0374	0.0356	0.0390	0.0412		
0.0202	0.0320	0.0207	0.0352	0.0220	0.0406		
$\Delta E^\circ = 0.0320$		$\Delta E^\circ = 0.0356$		$\Delta E^\circ = 0.0400$			
70 wt. % EC							
0.1069	0.0676	0.1080	0.0740	0.1143	0.0806		
0.0894	0.0674	0.0918	0.0738	0.0938	0.0802		
0.0703	0.0671	0.0701	0.0736	0.0731	0.0798		
0.0542	0.0668	0.0523	0.0732	0.0589	0.0788		
0.0400	0.0668	0.0383	0.0732	0.0206	0.0773		
0.0164	0.0666	0.0184	0.0730				
$\Delta E^\circ = 0.0665$		$\Delta E^\circ = 0.0727$		$\Delta E^\circ = 0.0761$			
with M = Li, Na, Rb & Cs, 25°C							
LiCl		NaCl		RbCl		CsCl	
$m(\text{mol kg}^{-1})$	ΔE	$m(\text{mol kg}^{-1})$	ΔE	$m(\text{mol kg}^{-1})$	ΔE	$m(\text{mol kg}^{-1})$	ΔE
10 wt. % EC							
0.2202	0.0137	0.1419	0.0042	0.1049	0.0017	0.1187	0.0002
0.1934	0.0124	0.1339	0.0036	0.0817	0.0015	0.0954	0.0002
0.1544	0.0096	0.1037	0.0023	0.0648	0.0013	0.0773	0.0
0.1192	0.0073	0.0893	0.0014	0.0450	0.0012	0.0581	0.0
0.0372	0.0022	0.0569	0.0002	0.0280	0.0010	0.0466	-0.0001
		0.0309	-0.0003			0.0220	-0.0002
$\Delta E^\circ = -0.0005$		$\Delta E^\circ = -0.0028$		$\Delta E^\circ = 0.0007$		$\Delta E^\circ = -0.0001$	
30 wt. % EC							
0.1539	0.0328	0.1446	0.0292	0.1008	0.0096	0.1217	0.0056
0.1215	0.0302	0.1172	0.0252	0.0796	0.0088	0.0932	0.0056
0.0978	0.0272	0.0954	0.0192	0.0597	0.0086	0.0726	0.0054
0.0719	0.0249	0.0764	0.0189	0.0394	0.0082	0.0554	0.0054
0.0480	0.0220	0.0642	0.0173	0.0260	0.0079	0.0374	0.0054
0.0244	0.0182	0.0317	0.0132			0.0175	0.0053
$\Delta E^\circ = 0.0170$		$\Delta E^\circ = 0.0080$		$\Delta E^\circ = 0.0075$		$\Delta E^\circ = 0.0052$	
50 wt. % EC							
0.1626	0.0499	0.1511	0.0556	0.1055	0.0284	0.1031	0.0216
0.1431	0.0496	0.1330	0.0538	0.0829	0.0282	0.0697	0.0216
0.1104	0.0496	0.1026	0.0520	0.0665	0.0275	0.0875	0.0216
0.0852	0.0496	0.0780	0.0506	0.0393	0.0271	0.0514	0.0215
0.0511	0.0495	0.0540	0.0486	0.0297	0.0270	0.0343	0.0215
0.0296	0.0488	0.0268	0.0464			0.0163	0.0214
$\Delta E^\circ = 0.0490$		$\Delta E^\circ = 0.045$		$\Delta E^\circ = 0.0268$		$\Delta E^\circ = 0.0213$	

(Contd)

Appendix: The observed emf values in volt of cell [A]: Ag-AgCl/MCl(*m*), Solvent/M(Hg)/MCl(*m*), Water/AgCl-Ag with M = Li, Na, Rb & Cs, 25°C—(Contd)

LiCl		NaCl		RbCl		CsCl	
<i>m</i> (mol kg ⁻¹)	Δ <i>E</i>	<i>m</i> (mol kg ⁻¹)	Δ <i>E</i>	<i>m</i> (mol kg ⁻¹)	Δ <i>E</i>	<i>m</i> (mol kg ⁻¹)	Δ <i>E</i>
70 wt. % EC							
0.1356	0.0922	0.1447	0.0920	0.1000	0.0584	0.1021	0.0526
0.1144	0.0920	0.1302	0.0914	0.0832	0.0584	0.0842	0.0524
0.0903	0.0919	0.0986	0.0910	0.0598	0.0580	0.0751	0.0522
0.0707	0.0920	0.0811	0.0906	0.0437	0.0576	0.0545	0.0520
0.0465	0.0920	0.0459	0.0902	0.0203	0.0566	0.0332	0.0520
0.0244	0.0918	0.0315	0.0898			0.0195	0.0518
Δ <i>E</i> ° = 0.0918		Δ <i>E</i> ° = 0.0088		Δ <i>E</i> ° = 0.0560		Δ <i>E</i> ° = 0.0514	

References

- (a) Kundu K K, De A L & Das M N, *J chem Soc Dalton*, (1972) 373, 378, 386; (b) Kundu K K, Rakshit A K & Das M N, *J chem Soc Dalton*, (1972) 381.
- Benetto H P & Spitzer J J, *J chem Soc Faraday Trans I*, 69 (1973) 1491.
- Bose K & Kundu K K, (a) *J chem Soc Faraday Trans I*, 73 (1977) 284; (b) *J soln Chem*, 8 (1979) 175; (c) *Indian J Chem*, 17A (1979) 122; (d) *Can J Chem*, 57 (1979) 2476.
- Das A K & Kundu K K, *Electrochim Acta*, 23 (1978) 685.
- Sivaprasad P & Kalidas C, *Adv Chem Soc*, (1979) 177, 395; *Trans SAEST* 19 (1980) and the relevant references therein.
- Halle J C & Bates R G, (a) *J chem Thermodyn*, 7 (1975) 999; (b) *J soln Chem*, 4 (1975) 1033; (c) 7 (1978) 245; (d) *J chem Soc Faraday Trans I*, 72 (1976) 2866.
- El-Harakany A A, Sadek S & Abdou A M, *Electrochimica Acta*, 26 (1981) 1677.
- Parker A J, *Chem Rev*, 69 (1969) 1.
- Bates R G, in *Solute-solvent interactions* edited by J F Coetzee and C D Ritchie (Marcel Dekker, New York, 1969).
- Marcus Y, *Ion-solvation*, (John Wiley, Chichester) (1985).
- Groves G S, Halawani K H & Wells C F, *J chem Soc Faraday Trans I*, 83 (1987) 1281.
- Wells C F, *Trans Faraday Soc* (a) 61 (1965) 2194; (b) 62 (1966) 2815; (c) 63 (1967) 147; (d) *Aust J Chem*, 36 (1983) 1739; (e) *Chem Soc Faraday Trans I*, 82 (1986) 2577.
- Cox B G, Hedwig G R, Parker A J & Watts D W, *Aust J Chem*, 27 (1974) 477.
- Marcus Y, *Pure appl Chem*, 58 (1986) 1721.
- (a) Basu-Mallick I N & Kundu K K, *Can J Chem*, 58 (1980) 79; (b) Das K, Das A K & Kundu K K, *Electrochim Acta*, 26 (1981) 47; (c) Das K, Bose K & Kundu K K, *Electrochim Acta*, 26 (1981) 479; (d) Bhattacharya A, Das A K & Kundu K K, *Indian J Chem*, 20A (1981) 347, 353; (e) Bhattacharya A, Datta J, Das K & Kundu K K, *Indian J Chem*, 21A (1982) 9; (f) Talukdar H, Rudra S P & Kundu K K, *Can J Chem*, 67 (1989) 321.
- Benetto H P, Feakins D & Lawrence K G, *J chem Soc (A)*, (1968) 1493.
- Sinha S, Guha P K & Kundu K K, *Z phys Chem NF*, Bd 167 (1991) 221.
- Blandamer M J & co-workers, *J chem Soc Faraday Trans I*, 82 (1986) 1471.
- (a) Rudra S P, Talukdar H & Kundu K K, *Can J Chem*, 65 (1987) 2595; (b) Bhattacharya S, Mandal U & Kundu K K, *Z phys Chem NF*, Bd 167 (1990) S 47; (c) Rudra S P, Chakravorty B P, Kundu K K & Basu-Mallick I N, *Z phys Chem NF*, Bd 150 (1986) S 211 and the relevant references therein.
- Datta J, Bhattacharya A & Kundu K K, *Bull chem Soc Japan*, 61 (1988) 1735.
- Pierotti R A, *Chem Rev*, 76 (1976) 717.
- Born M, *Z Physik*, 1 (1920) 45.
- Kim J I (a) *J phys Chem*, 82 (1978) 191; (b) Kim J I, Cocal A, Born H J & Comma F A, *Z phys Chem NF*, 110 (1978) S 209.
- Blandamer M J, Burgess J, Hamshire S J & Mearns F M, *Trans metal Chem*, 4 (1979) 77.
- Popovych O, *Anal Chem*, 46 (1974) 2009; Popovych O, Gibofsky A & Barne D H, *Anal Chem*, 44 (1972) 811.
- Pearson R G, *J Am chem Soc*, 85 (1963) 3533.
- Feakins D & Voice P J, *J chem Soc Faraday Trans I*, 68 (1972) 1390.
- Das A K & Kundu K K (a) *J chem Soc Faraday Trans I*, 70 (1974) 1452; (b) *J soln Chem*, 4 (1975) 431.
- (a) Juillard J, *J chem Soc Faraday Trans I*, 78 (1982) 43; (b) Juillard J, Tissier C, Barzyliska J, Makrzan J & Taniewska-Osinska S, *J chem Soc Faraday Trans I*, 81 (1985) 3081.
- Biswas P K & Das M N, *J chem Soc Faraday Trans I*, 82 (1986) 1973.
- Fuchs R, Hagen C P & Rodewald R F, *J phys Chem*, 78 (1974) 1509.
- Miyaji K & Morinaga K, *Bull chem Soc Japan*, 58 (1986) 1695.
- Cox B G, Natarajan R & Waghorne W S, *J chem Soc Faraday Trans I*, 75 (1979) 86.
- Booj M & Somsen G, *Electrochim Acta*, 28 (1983) 1883.
- Abraham M H, Hill T, Ling H C, Schulz R A & Watt R A C, *J chem Soc Faraday Trans I*, 80 (1984) 489.
- (a) Kundu K K, *Indian J Chem*, 10 (1972) 303; (b) Bose K, Das A K & Kundu K K, *J chem Soc Faraday Trans I*, 74 (1978) 1051 and the relevant references therein; (c) Kundu K K & Mazumdar K, *J chem Soc Faraday Trans I*, 69 (1973) 806.
- Datta J & Kundu K K, *J phys Chem*, 86 (1982) 4055.
- Wicke E, *Angew Chem*, 5 (1966) 106.
- Desnoyers J E & Joliceur C in *Modern aspects of electrochemistry* edited by J O'M Bockris & B E Conway, No. 5, (Plenum Press, New York) 1969.